REPORT DOCUMENTATION PAGE	Form Approved OMB NO. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comment regarding this burden estimates or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 2/13/98	3. REPORT TYPE AND DATES COVERED Final Progress Report 9/29/94–9/29/97

4. TITLE AND SUBTITLE Etching Chemistry of III-V Semiconductors and the Development of Surface Roughness	5. FUNDING NUMBERS DAAH04-94-G-0410

6. AUTHOR(S)

Jory A. Yarmoff

7. PERFORMING ORGANIZATION NAMES(S) AND ADDRESS(ES) Department of Physics University of California Riverside, CA 92521	8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211	10. SPONSORING / MONITORING AGENCY REPORT NUMBER ARO 32572.10-PH

11. SUPPLEMENTARY NOTES

The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

12a. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

19980519 110

13. ABSTRACT (Maximum 200 words)

This research addresses the need for fundamental information concerning halogen etching of III-V semiconductors. The reactions of halogens with semiconductor surfaces are the fundamental chemical interactions in processes employed for device manufacture. In this work, the reactions of XeF_2, Cl_2 and I_2 with III-V semiconductor surfaces were investigated with synchrotron-based soft x-ray photoelectron spectroscopy, low energy electron diffraction and scanning tunneling microscopy. Fluorine reaction grows films of group III fluorides, which can be used as dielectric materials. Chlorine is the most widely used halogen for dry etching, while iodine has been proposed for use as a "gentle" etchant. We found that, for all of the halogen reactions, the initial adsorption depends on the surface reconstruction, stoichiometry and condition. Some surfaces passivate, while others spontaneously etch at room temperature. The passivated surfaces are well-ordered and covered with approximately one monolayer of adsorbed halogen. The etched surfaces, on the other hand, are considerably rough and atomically disordered. A microscopic model is proposed which assumes that halogen atoms preferentially adsorb onto a group III atom if the surface is initially well-ordered. This microscopic model can explain why certain surfaces etch, while others form ordered overlayers.

14. SUBJECT TERMS Semiconductor processing, etching, gallium arsenide, III-V Semiconductors, Surface Chemistry, Surface Physics	15. NUMBER IF PAGES 8
	16. PRICE CODE

17. SECURITY CLASSIFICATION OR REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL

FINAL TECHNICAL REPORT

A. STATEMENT OF THE PROBLEM STUDIED

This research addressed the need for fundamental information concerning halogen etching of III-V semiconductors. The chemical reaction of atomic and molecular halogens with semiconductor surfaces is the major component of most dry processes employed for device manufacture. Most often, processes such as reactive ion etching and chemical vapor deposition, are optimized by empirically balancing requirements for smooth surfaces and high etch rates, with little knowledge of the surface chemistry on the microscopic scale. By providing a fundamental understanding of the relevant surface chemistry, it will be possible to optimize current processes and to design new ones in a more efficient manner. The information obtained from this research is also critical for the development of new types of processes, such as atomic layer epitaxy (ALE), that are designed to produce atomic-scale structures.

There have been many fundamental studies of halogen reactions with Si, due to the predominance of Si technology and because Si is relatively easy to work with. GaAs and other III-V semiconductors do play a large role in the semiconductor industry, however, particularly in optoelectronic devices. Furthermore, because of the increased mobility of electrons in these materials, they have the potential for use in ultra-high speed devices. The biggest drawback to the use of these materials, however, has been their processibility. Thus, more fundamental research is necessary in order to solve the materials science problems associated with the etching and growth of III-V semiconductors.

A large problem encountered when working with these materials is that the surface structure and stoichiometry can vary considerably from one sample to another. It is therefore difficult to reproducibly prepare samples. Thus, one goal of this program was to develop methods for systematic preparation of surfaces with known structure. As shown below, we have identified some very specific treatments that lead to particular, well-ordered surface structures.

Furthermore, it has been found that for certain surface structures, halogen adsorption at room temperature results in the formation of a stable, well-ordered overlayer, while for other surfaces spontaneous etching occurs. Samples etched in this manner are macroscopically rough, and have disordered surfaces containing many defects. Thus, another goal of this program was to understand the fundamental reasons why certain surfaces etch and others don't. We believe we have identified one of the major factors governing this behavior, and have proposed a microscopic mechanism for the loss of surface order during halogen reaction.

We carried out experimental investigations of the reactions of XeF_2 [1-2], Cl_2 [6-8, 10], and I_2 [3-5, 11] with particular III-V semiconductor surfaces. The research made use of the tools of surface science to investigate fundamental aspects of a "real" problem. In particular, we used synchrotron-based soft x-ray photoelectron spectroscopy (SXPS), low energy electron diffraction (LEED) and scanning tunneling microscopy (STM). During this time, we also wrote a review article [9] that reported on the current state of the field. We showed how many techniques can be used together to solve such surface chemical problems. From these many results, a basic pattern underlying halogen/III-V semiconductors reactions is emerging, although more work is still needed to complete the picture.

B. SUMMARY OF THE MOST IMPORTANT RESULTS

Fluorine is not normally used as an etchant for III-V materials, due to the involatility of group III metal fluorides. The reaction does have microelectronics applications, however, as it can be used to grow films of group III fluorides for use as dielectric materials. Furthermore, and perhaps more importantly, it is useful to study fluorine reactions as part of a comprehensive fundamental investigation, since fluorine is the most reactive of the halogens. The room temperature reaction of XeF_2 with GaAs produces films of solid GaF_3, which is a 10 eV bandgap insulator, while the excess As is removed from the surface. The reaction therefore involves simultaneous film growth and etching. This is a convenient manner in which to grow insulating films on III-V semiconductor substrates, as it simply involves reacting the substrate in vacuum with a gas, in an analogous manner to SiO_2 growth on silicon by reaction with O_2. We investigated the evolution of the insulator/semiconductor interface with film growth [1] and the effects of surface temperature on the reaction [2]. Figure 1 shows Ga and As 3d SXPS data, which were collected at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, for XeF_2 reactions with GaAs(110). These data show that there is an interface region between the GaF_3 film and the substrate, consisting of GaF, AsF and tri-coordinate Ga and As atoms. Group III and V elements are stable in tri-coordinate configurations, which form as bonds break in the near-surface region. We showed that the thickness and composition of the interface region is independent of the film thickness. Measurements of samples that were reacted with XeF_2 at ~600 K, which is above the decomposition temperature of GaF_3, showed that Ga and As are removed stoichiometrically, while a thin film (~1 atomic layer) of elemental As remains on the surface [2]. These results indicate that the interaction of fluorine with GaAs is a frustrated etching reaction, which is a consequence of the low volatility of Ga fluorides.
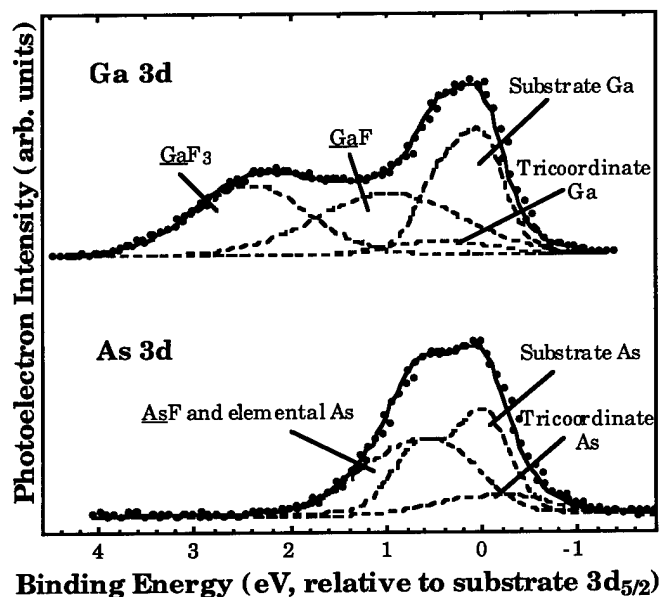

Figure 1. Background-subtracted, high-resolution SXPS spectra of Ga and As 3d core levels, collected from GaAs(110) after reaction with sufficient XeF_2 to produce a 4 Å thick film of GaF_3. The experimental data are shown along with numerical fits to the data, and each component is identified.

Chlorine is the halogen most widely used in device manufacture. We completed investigations of the Cl_2 reaction with GaAs, and began to look at Cl_2 reactions with other substrates, as well. Cl_2 adsorbs dissociatively on GaAs, and can spontaneously etch the substrate under certain conditions. We investigated the effects of the initial surface structure [7], substrate temperature [6], and exposure level [8]. The adsorption pathway is dependent on the clean surface reconstruction and condition [7]. Ga-rich surfaces are initially more reactive than As-rich surfaces. The initial adsorption kinetics are described by the Elovich equation, i.e., the sticking coefficient for Cl_2 decays exponentially with the amount of adsorbed Cl.

Although GaAs surfaces appear to passivate after the initial exposures to Cl_2 at room temperature, they begin to etch after larger exposures. In the early stages of etching, Ga is preferentially removed from the surface. The etching reaction ultimately produces volatile $AsCl_3$ and $GaCl_3$, which form through the stepwise addition of Cl. After sufficient Cl_2 exposure to attain steady-state etching, the surfaces are terminated by -AsCl-GaCl$_2$ "tree"-like structures. SXPS spectra collected from such a surface are shown in Fig. 2 [8]. The surfaces are very rough and contain buried tri-coordinate atoms, in a similar manner as the interfaces produced by fluorine reaction. Such "tree" structures, and the associated disorder, are likely to be involved in Cl_2 reactions with other III-V surfaces, as well. The addition of the final Cl atom in forming gaseous $GaCl_3$ was identified as the rate-limiting step in the overall etching reaction.
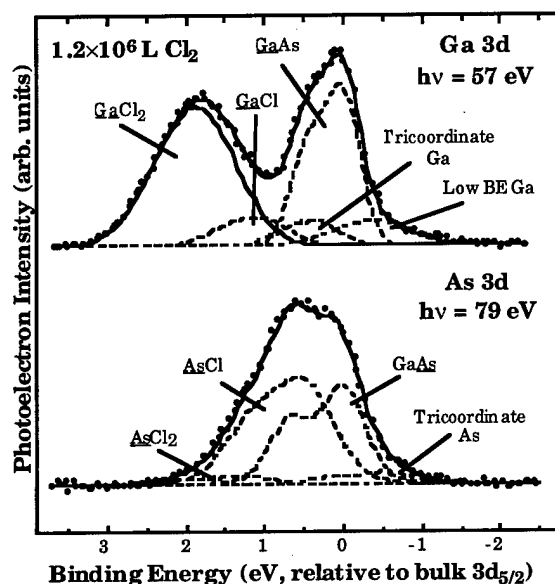

Figure 2. Background-subtracted, high-resolution SXPS spectra of Ga and As 3d core levels, collected from GaAs(110) after a prolonged reaction with Cl_2. The experimental data are shown along with numerical fits to the data. From ref. [8].

There is a correspondence between the gas phase and surface products formed at different temperatures, which allows for the microscopic reaction mechanism to be modeled. At low temperatures, the gaseous products are the tri-chlorides and the surface products are the intermediate mono- and di-chlorides. At higher temperatures, the gaseous products are GaCl and As dimers and tetramers. Accordingly, we found that at temperatures between 500 and 600 K, the surfaces are etched by Cl_2 and the resultant surface layer is composed of elemental As and contains no chlorine [6], in a similar manner as the high temperature fluorine reaction. For reaction at temperatures above 600 K, stoichiometric etching is observed, which produces clean GaAs surfaces with a very high degree of crystallinity. Reaction with Cl_2 at elevated temperature is thus one way in which clean, well-characterized and well-ordered GaAs surfaces can be reproducibly prepared without the need for complex procedures, such as molecular beam epitaxy (MBE).

We recently began to investigate the reaction of Cl_2 with InAs(001) [10]. We first looked at the reaction with the In-terminated c(8×2) surface, which is produced by Ar sputtering and annealing in vacuum. We then used the adsorption and subsequent removal of iodine (see below) to produce the As-terminated c(2×8) structure, and reacted that surface with Cl_2. Figure 3 shows In 4d and As 3d spectra collected after typical exposures of each surface. We see that although the largest reaction occurs with the element that terminates the surface, Cl_2 does in fact react with both elements. From this, we conclude that the reaction is very similar to that of Cl_2 with GaAs, in that (1) substrate bonds are broken, i.e., etching can occur at room temperature, and (2) the details of the reaction depend on the initial surface stoichiometry.
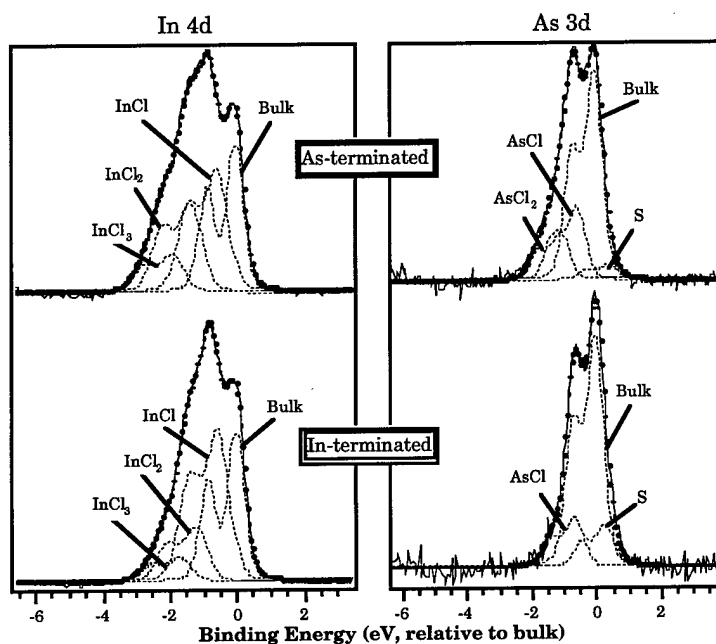
3

Figure 3. Background-subtracted, high-resolution In 4d and As 3d SXPS spectra collected following exposure of the In-terminated InAs(001)-c(8×2) surface and the As-terminated InAs(001)-c(2×8) surface to Cl_2. The experimental data are shown along with numerical fits to the data.

Iodine can also etch III-V semiconductors, and has been proposed for use as a more "gentle" etchant than chlorine. We investigated the reaction of I_2 with GaAs, InAs and InSb (001) surfaces. For low exposures at room temperature, I_2 forms very highly ordered 1×1 structures [3-5]. We investigated the dispersion of the surface electronic states of these structures [5], the chemical reactions of I_2 with the substrates [3], and the order within the iodine overlayers [4]. The ordered structures involve minimal disruption of the substrate, as iodine simply bonds to the outermost surface atoms. The 1×1 ordered overlayers have a state located at ~4.4 eV below the valence band maximum, which shows a dispersion within a 1×1 surface Brillouin zone, and passes through an open lens in the projected bulk density of states [5]. While GaAs and InAs become saturated with iodine at room temperature, inhibiting further reaction, InSb is etched via the preferential loss of In. When all of the iodine-covered surfaces are annealed, however, the group III element is preferentially removed, producing a group V-terminated surface. This result thus suggests a means whereby a single atomic layer can be removed via a surface chemical reaction. This "atomic layer etching" process can also be exploited to reproducibly produce certain surface structures that previously required the use of MBE. Both I 4d SXPS spectra and STM images collected from the ordered surfaces show two types of iodine [4]. These types may be related to iodine bound to broken and unbroken surface dimer atoms, as illustrated in Fig. 4. More work is currently underway to verify this.
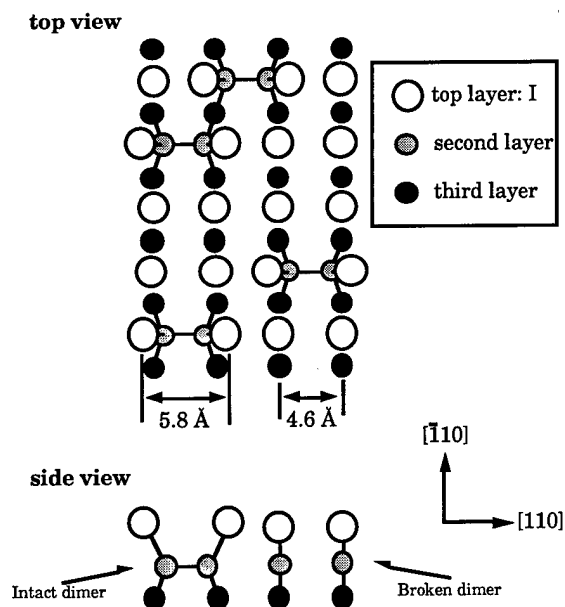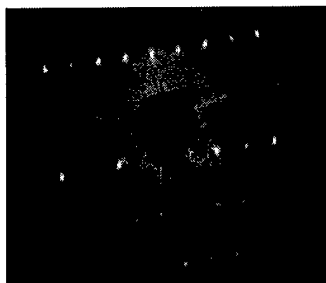
top view

○	top layer: I
◉	second layer
●	third layer

5.8 Å   4.6 Å

[Ī10]

[110]

side view

Intact dimer   Broken dimer

Figure 4. Schematic diagram illustrating the proposed structure of an iodine-covered (001)-1×1 III-V semiconductor surface. The structure involves iodine bonded to the outermost surface atoms, some of which are still dimerized, as on the clean surface, while others have had that dimer bond broken.
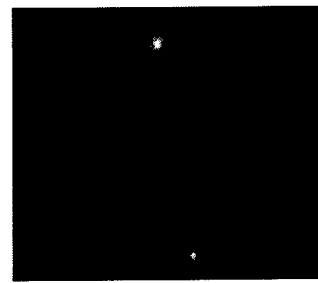
It has been observed that some III-V surfaces etch, while others form ordered overlayers. A careful study, in which we compared I_2 reaction with two different InAs(001) reconstructions, has lead to a microscopic model of halogen/III-V reactions [11]. The utility of this experiment was that a single material could be prepared so to it either passivated or etched, depending on the details of the structure. We found that on the In-terminated c(8×2) surface, a sharp 1×1 LEED pattern formed following I_2 exposure, indicating that the surface was highly-ordered. SXPS indicated that all of the iodine was singly coordinated to surface In atoms, i.e., none was bonded to As. On the As-terminated c(2×8) surface, on the other hand, the surface became highly disordered by the reaction, and iodine was bonded to both In and As. The LEED results are shown in Fig. 5 and some representative SXPS data are shown in Fig. 6.

5

Figure 5. The evolution of the LEED patterns for I_2 reacted with InAs(001). (a) The clean, well ordered c(8×2) surface produced by Ar+ sputtering and annealing. This LEED pattern indicates that the surface is In-terminated. (b) The sharp 1×1 pattern produced by I_2 reaction with the c(8×2) surface. This pattern shows that an ordered structure is formed. (c) The c(2×8) pattern produced by annealing an I_2-saturated surface. This pattern indicates that the surface is As-terminated. (d) The LEED pattern is removed following I_2 reaction with the As-terminated surface, indicating surface disordering.
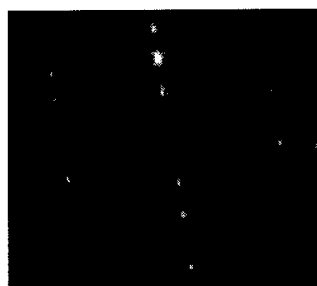

(a) In-terminated c(8×2)

(b) I_2 reacted c(8×2)

(c) As-terminated c(2×8)

(d) I_2 reacted c(2×8)

In 4d

As 3d

InI

Bulk

InI$_2$

I_2/c(8×2)

S$_1$

Bulk

S$_2$

Intensity (arb. units)

InI

Bulk

InI$_2$

I_2/c(2×8)

AsI

AsI$_2$

Bulk

S$_2$

-4   -2   0   2   -4   -2   0   2
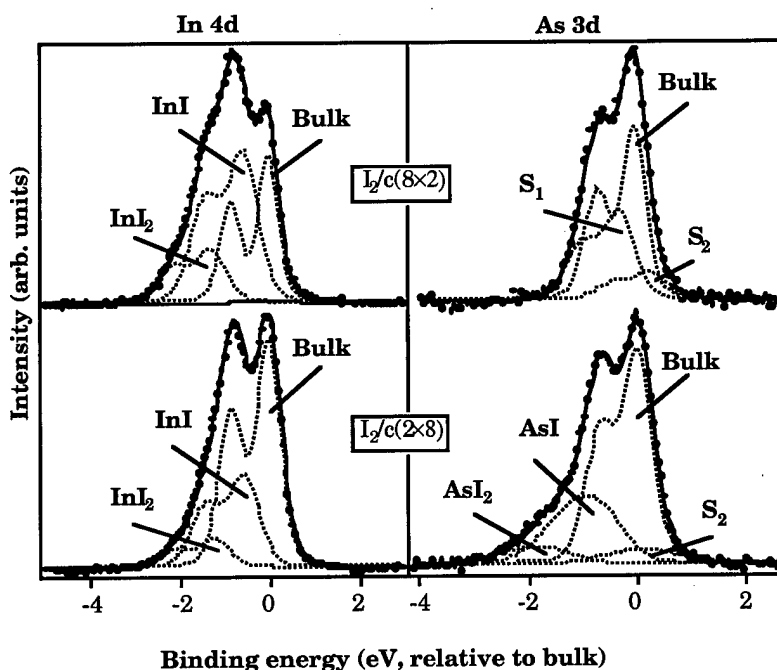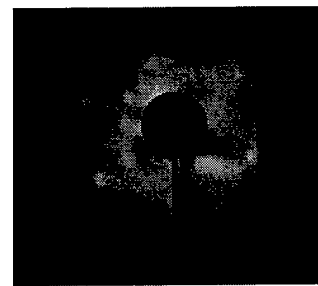
Binding energy (eV, relative to bulk)

Figure 6. Soft x-ray photoelectron spectra collected from InAs(001) following reaction with I_2. The upper panels show the In-terminated surface, while the bottom panels show the As-terminated surface. These data show that the In-terminated surface forms only In iodides, while the As-terminated surface forms both In and As iodides.

6

The microscopic model that explains these observations is based on the assumption that iodine will preferentially react with group III (i.e., In) atoms, as opposed to group V elements. A schematic of the InAs(001) surfaces is shown in Fig. 7. On the well-ordered clean surface, the group III atoms have an empty orbital extending into the vacuum, while the group V atoms have a filled orbital, i.e., a lone pair of electrons. There will be some repulsion between the lone pair of a group V atom and the valence electrons of the incoming I_2, while there will be attraction between the unoccupied orbital of a group III atom and the I_2 molecule. This idea has been suggested by some previous theoretical work, so it is not surprising that this preference for reaction with the group III element exists. For the In-terminated surface, reaction therefore occurs with the outermost atoms and the structure remains well-ordered. On the group V-terminated surface, however, the reaction most likely occurs at a group V element located in the second layer in one of the missing rows. When an iodine bond is formed with a second layer atom, it will withdraw charge from the first layer group V atom. This will deplete the surface lone pair, thereby making the outermost group V more reactive to I_2. Thus, after sufficient reaction to observe iodine bonding with SXPS, I is attached to both In and As. This scenario enables substrate bonds to be weakened and to then break, which ultimately leads to etching. Thus, this microscopic model can explain why with some surfaces, halogen reaction produces an ordered overlayer, while other surfaces become disordered and etch.
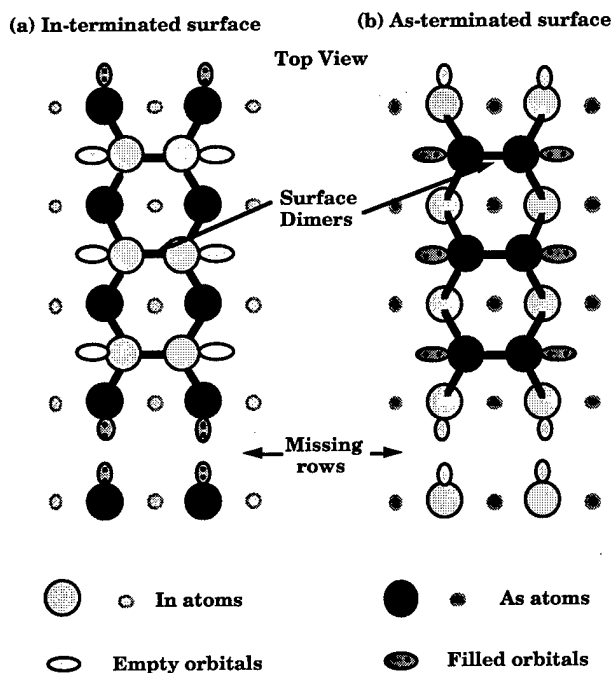

Figure 7. Schematic of the In-terminated and As-terminated InAs(001) surfaces, showing the surface dimers, the empty orbitals associated with surface In atoms, and the filled, lone-pair orbitals associated with surface As atoms.

In summary, an experimental program probing the basic surface chemical reactions of halogens with III-V semiconductor surfaces has been completed. Much has been learned about the surface chemical products formed, the kinetics of the reactions, and the structures of the resulting surfaces. In addition, we learned how to exploit these reactions for the production of novel surface structures. Finally, a microscopic understanding of these reactions is beginning to form.

C. LIST OF ALL PUBLICATIONS AND TECHNICAL REPORTS

1. W.C. Simpson, T.D. Durbin, P.R. Varekamp and J.A. Yarmoff, "The Growth of GaF_3 Films on GaAs(110) at Elevated Temperatures Studied with Soft X-ray Photoelectron Spectroscopy", J. Appl. Phys. **77**, 2751-2758 (1995).

2. W.C. Simpson, P.R. Varekamp, D.K. Shuh and J.A. Yarmoff, "Soft X-Ray Photoelectron Spectroscopy Study of the Reaction of XeF_2 with GaAs", J. Vac. Sci. Technol. A **13**, 1709-1713 (1995).

3. P.R. Varekamp, M.C. Håkansson, J. Kanski, D.K. Shuh, M. Björkqvist, M. Göthelid, W.C. Simpson, U.O. Karlsson and J.A. Yarmoff, "Reaction of I_2 with the (001) surfaces of GaAs, InAs, and InSb; I. Chemical interaction with the substrate", Phys. Rev. B **54**, 2101-2113 (1996).

4. P.R. Varekamp, M.C. Håkansson, J. Kanski, M. Björkqvist, M. Göthelid, B.J. Kowalski, Z.Q. He, D.K. Shuh, J.A. Yarmoff and U.O. Karlsson, "Reaction of I_2 with the (001) surfaces of GaAs, InAs, and InSb; II. Ordering of the iodine overlayer", Phys. Rev. B **54**, 2114-2120 (1996).

5. P.R. Varekamp, M.C. Håkansson, J. Kanski, B.J. Kowalski, L.Ö. Olsson, L. Ilver, Z.Q. He, J.A. Yarmoff and U.O. Karlsson, "Angle-resolved photoemission spectroscopy of the 1x1 ordered overlayers on iodine-saturated GaAs(001) and InAs(001)", Surf. Sci. **352/354**, 387-390 (1996).

6. W.C. Simpson, W.M. Tong, C.B. Weare, D.K. Shuh and J.A. Yarmoff, "The Temperature Dependence of the Cl_2/GaAs(110) Surface Product Distribution", J. Chem. Phys. **104**, 320-325 (1996).

7. W.C. Simpson, D.K. Shuh, W.H. Hung, M.C. Håkansson, J. Kanski, U.O. Karlsson and J.A. Yarmoff, "The Role of Surface Stoichiometry in the Cl_2/GaAs(001) Reaction", J. Vac. Sci. Technol. A **14**, 1815-1821 (1996).

8. W.C. Simpson, D.K. Shuh and J.A. Yarmoff, "Room Temperature Chlorination of As-Rich GaAs(110)", J. Vac. Sci. Technol. B **14**, 2909-2913 (1996).

9. W.C. Simpson and J.A. Yarmoff, "Fundamental Studies of Halogen Reactions with III-V Semiconductor Surfaces", Ann. Rev. Phys. Chem. **47**, 527-554 (1996).

10. W.K. Wang, W.C. Simpson and J.A. Yarmoff, "Photoemission Studies of the Chemisorption of Cl_2 on InAs(001)", National Synchrotron Light Source Annual Report 1997 (one page).

11. W.K. Wang, W.C. Simpson and J.A. Yarmoff, "Passivation versus Etching: Adsorption of Iodine on InAs(001)", in preparation.

D. PARTICIPATING SCIENTIFIC PERSONNEL

Name	Position	Degree awarded
Jory A. Yarmoff	PI	
Patrick R. Varekamp	Graduate Student	Ph.D. awarded 9/95
William C. Simpson	Graduate Student	Ph.D. awarded 12/95
Wei K. Wang	Graduate Student	